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**ELECTRONIC STUDY OF Pt-Ga INTERMETALLIC COMPOUNDS  
USING X-RAY PHOTOEMISSION SPECTROSCOPY**

by

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submitted to

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**Electronic structure study of Pt-Ga intermetallic thin films using  
X-ray photoemission spectroscopy**

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Single-phase films of Pt-Ga intermetallic compounds with different stoichiometric compositions were grown using molecular beam epitaxy (MBE) and investigated with X-ray photoemission spectroscopy (XPS). The qualitative aspects of the peak shifts and shapes are consistent with those of other compounds that have been previously investigated. Semi-quantitative analyses show that the valence bands are dominated by Pt-Ga hybridization, rather than Pt d-d interactions, and that final state effects dominate initial state charge transfer in determining the binding energies (BE) of the Pt core level peaks.

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Several Pt-Ga intermetallic compounds are good candidates for contacts on III-V compounds because of their thermodynamic stability with respect to these semiconductors.<sup>1</sup> For example, a conducting contact of PtGa<sub>2</sub> is thermodynamically stable on GaAs, whereas elemental Pt is not.<sup>2</sup> They also have interesting electronic properties which provide a good model to study the evolution of d-bands in complex lattices, since Ga contributes only sp states of the valence band (VB) of the compounds.

Similar Pt-metalloid alloys have been studied by several groups using XPS, such as the Pt-Sn and Pt-Pb solid solutions reported by Cheung<sup>3</sup> and the Pt-Cd and Pt-Au solid solutions studied by Shevchik.<sup>4</sup> Their results are summarized as follows: as the Pt concentration decreased, (i) the Pt d-band became narrower and moved to higher binding energy; (ii) the density of states (DOS) at the  $E_F$  decreased and the Pt 4f line shape was more symmetric, except for the Pt-Au alloy.

The state of a d-electron in an sp-band metal is generally described by the Friedel-Anderson virtual bound state model, which treats the d-orbital in the Hartree-Fock approximation as residing energetically in the sp-conduction bands (CB).<sup>5,6</sup> In order to explain the Pt concentration dependence of the 5d VB in solid solutions, Schevchik proposed a simple molecular orbital model which included the effects of overlap on adjacent atoms.<sup>7</sup> An alternative explanation was made by Cheung,<sup>3</sup> using the multiple scattering theory of Anderson and McMillan.<sup>8</sup> These two explanations emphasize the prominent role of like-neighbor interactions in alloys that were first pointed out by Friedel.<sup>9</sup>

However, several studies of compounds of transition and polyvalent metals, such as  $\text{NiSi}_2$ ,  $\text{AuAl}_2$ ,  $\text{AuGa}_2$ ,  $\text{AuIn}_2$  and  $\text{PtGa}_2$ , have shown that the evolution of d-bands of these compounds results primarily from the effects of hybridization of d-bands with the sp-bands.<sup>10-12</sup> In addition, a simple tight-binding model of the 3d transition metal-polyvalent metal compounds and alloys, such as,  $(\text{Fe, Co, Ni})_x\text{Al}_{1-x}$  and  $\text{Co}_x\text{Ga}_{1-x}$ , have confirmed that the large mixing between the d-states of the transition metal and sp-states of the polyvalent metal and the resulting strong short-range order are the main factors governing the electronic structures of these compounds.<sup>13</sup> Since Pb, Sn, Cd, and Ga have almost the same electronegativities and work functions, as shown in Table I,<sup>14</sup> the electronic properties of the Pt-Ga intermetallic compounds should be very similar to those of Pt-Sn, Pt-Pb, and Pt-Cd solid solutions.

The Pt-Ga intermetallic compounds have well known crystal structures. Therefore, the actual Pt-Pt interatomic distances and the coordination number (CN) of Pt in each of the intermetallic films are known. In general, XPS core-level BE chemical shifts can be related to the amount of charge transfer between the atoms, and the charge transfer is usually small in intermetallic compounds.<sup>15,16</sup> Recently, an XPS study of a series of Ni-Ga and Ni-In intermetallic compounds showed that there are no large chemical shifts due to charge transfer between the atoms.<sup>17</sup> As shown in Table I, the electronegativity differences between Ni and Ga or In are 0.3, but the electronegativity difference between Pt and Ga is 0.6.<sup>18</sup> Thus, one should expect

a much more significant charge exchange to occur in Pt-Ga compounds compared to Ni-Ga compounds. In this study, the XPS spectra of the VB and core levels of three different Pt-Ga intermetallic compounds have been collected to investigate the relative contribution of d-d interactions to the evolution of d bands and to determine if chemical shifts in the intermetallic compounds scale with electronegativity.

The Pt-Ga intermetallic thin films were grown on GaAs (100) by co-deposition of the elements in a MBE chamber with a base pressure of  $2 \times 10^{-9}$  Torr. An electron beam evaporator and a Knudsen cell were used to produce the Pt and Ga beams, respectively. Elemental Pt and Ga films were also grown with these two sources. The details of the thin film growth can be found elsewhere.<sup>2</sup> Phase identification of these thin films were determined with X-ray powder diffractometry (XRD). The XRD patterns showed that all these films were single phase. The photoemission spectra were measured with a Kratos ES 800 spectrometer, featuring non-monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) in ultrahigh vacuum (base pressure  $\sim 5 \times 10^{-10}$  Torr). The total experimental resolution was estimated to be about 1.4 eV. The samples were cleaned by several cycles of sputtering with Ar ions (3 keV, 20 mA). The XPS spectra were collected with the sample normal to the electron energy analyzer to minimize the surface contributions to the spectra. The relative intensities of the Pt 4d and Ga 3d lines were measured and the compound composition within the photoelectron emission depth after ion

bombardment was calculated from theoretical cross sections.<sup>19</sup> This calibration agreed with the starting stoichiometry of the elements in each sample to within 8% in the worst case for the Pt-Ga systems.<sup>20</sup> In this calculated stoichiometry, as the Pt concentration decreases, the deviation from the expected stoichiometry becomes larger, which means that preferential sputtering of Ga atoms probably occurred during ion bombardment. The level of contamination was estimated from the intensity of the O 1s and C 1s XPS peaks relative to Ga 3d peak. The combined O and C contamination on the surface was less than 1 at. % for the Pt-Ga thin films in the XPS sample depth.

The XPS VB spectra for elemental Pt, Ga, and the Pt-Ga intermetallic thin films are presented in Fig. 1. The core level spectra presented in Fig. 2 are normalized to the same height of the peaks of interest after removal of the Al  $K\alpha_{3,4}$  satellites. The peak positions and bandwidths are also given in Table II. The BE scales for the core level spectra are referred to the  $E_F$  of each film. The  $E_F$  was assigned by locating the spectral position on the leading edge of the VB that was 12% of the maximum intensity and then moving to higher BE by one-half of the FWHM of the broadening function, which was taken to be 1.4 eV. The core level spectra of the Pt 4f spin-orbit split doublet and the Ga 3p and 3s levels in the Pt-Ga intermetallic compounds are shown in Fig. 2. In order to facilitate their comparison, the spectra have been aligned with respect to the  $4f_{7/2}$  level of Pt. The BE values for the Ga 3s, 3p, and Pt 4f core levels with respect to the  $E_F$  of the Pt-Ga intermetallic compounds are summarized in Table III.

Fig. 1 shows that the Pt d-band widths decreased with decreasing Pt concentration. The band widths can be analyzed in terms of the following: (1) lifetime broadening, (2) spin-orbit splitting, (3) variation of interatomic distances, (4) variation of number of Pt-Pt nearest-neighbor interactions, and (5) hybridization of the Pt d-band with the Ga sp-band. The effects due to lifetime broadening and spin-orbit coupling are large but essentially constant for all the compounds, so we will concentrate on the last three effects.

Anderson has shown that the interatomic d-hopping integrals, and hence the d band widths of metallic elements, are inversely proportional to the fifth power of the distance between the atoms in the absence of hybridization.<sup>21</sup> Watson *et al.* have also demonstrated that the d-band width depends on the interatomic distance with an exponent between  $R^{-3.2}$  and  $R^{-5}$  for transition metals.<sup>22</sup> Therefore, we need consider only nearest-neighbor interactions here. In addition, in the tight-binding approximation, for a given atomic distance, the band width is proportional to the coordination number. In order to apply these rules to the intermetallic thin films, we must consider the individual crystal structures of the thin films and the Pt-Pt nearest-neighbor interactions, which are given in Table IV.

First, consider the comparison of elemental Pt and  $\text{Pt}_2\text{Ga}$ . The Pt-Pt distance does not change, but the coordination number decreases by almost a factor of two, which should result in a factor of two decrease in the Pt d-band width if d-d interactions dominate. In the case of Pt and  $\text{PtGa}_2$ , the Pt-Pt distance is 1.5 times longer in the compound, so that even if the band width is



inversely proportional to only the third power of the Pt-Pt distance, one would expect the Pt d-band width to decrease by a factor of about 3. Thus, the Pt d-band widths should decrease dramatically with decreasing Pt concentration in the compounds. However, Table II shows that the Pt d-band width changes are much smaller than those indicated above. These results indicate that the coordination and Pt-Pt distances cannot explain the observed Pt d-band width. Thus, factors other than Pt-Pt interactions are also important in determining the d-band width changes. We believe that the major factor is the hybridization between the Pt d-band and the Ga sp-band of these compounds. The semiempirical band structures of Pt and PtGa<sub>2</sub> were calculated by Kim *et al.* using a mixed-basis band-structure interpolation scheme (MBBSIS).<sup>12</sup> In these calculations, the d-band width of PtGa<sub>2</sub> was narrower than that of Pt, because the d bands reside in a band gap of the sp bands. Similar studies of AuGa<sub>2</sub> and AuIn<sub>2</sub> compounds also confirmed that mixing of the d-bands with an sp-band is a main factor governing the evolution of d-band widths.<sup>10,11</sup>

Transition metal XPS line shapes depend upon excitations of electron-hole pairs at  $E_F$  that result from the screening of the core hole left by the photoemission events and the asymmetry increases with the local joint DOS for electron-hole pair excitations.<sup>23</sup> For Pt metal, 5d electrons are mainly responsible for the screening of the 4f core hole<sup>24</sup> because the 5d band crosses the  $E_F$ . The decrease in the DOS at the  $E_F$  with increasing Ga concentration of the compounds shown in Fig. 1 leads to the decrease of the Pt 4f line

asymmetry shown in Fig. 2.

XPS core level chemical shifts are determined by both initial and final state effects. The former is due to the chemical bonding in the compounds (charge transfer between the atoms) and the latter is due to changes in the screening of the core hole.<sup>25</sup> With increasing dilution of Pt, the increasing relative BE shift of the Pt 4f core level from the Ga 3p core level in Fig. 2 results primarily from the absolute shift of the Pt 4f core level to higher BE, since the BEs of the Ga 3d core level for each of the Pt-Ga intermetallic compounds in Fig. 1 remain almost unchanged. Thus, the final state effects, i.e. less efficient screening of the core hole with decreasing DOS at the  $E_f$ , which shift the Pt 4f core level to higher BE, are dominant. The initial state effects that would be expected to shift the Pt 4f core level to lower BE are smaller even though the electronegativity difference between Pt and Ga is quite large, with Pt the more electronegative (Table I).

XPS VB and core level spectra of three Pt-Ga intermetallic thin films of various stoichiometric compositions have been investigated. With decreasing Pt concentration, the Pt d-band width decreases, but not as dramatically as one would expect if d-d interactions dominated the band width. Thus, hybridization with the Ga sp-bands appears to be important for these compounds. Even though the electronegativity of Pt is much larger than that of Ga, the Pt core-level peaks are shifted to higher BE in the compounds. This shows that final state effects dominate the energies at which the Pt peaks appear in the spectra.

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  20. The compound compositions within the XPS sampling depth ( $\sim 20\text{\AA}$ ) calculated from the Pt 4d and Ga 3d intensities and the theoretical cross section of Ref. 18 are as follows;  $\text{Pt}_2\text{Ga}$  ( $\text{Pt}_{0.68}\text{Ga}_{0.32}$ ),  $\text{PtGa}$  ( $\text{Pt}_{0.56}\text{Ga}_{0.44}$ ),  $\text{PtGa}_2$  ( $\text{Pt}_{0.41}\text{Ga}_{0.59}$ ), where the compositions inside the parentheses are the ones obtained from XPS peak intensities.
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TABLE I. Comparison of values of work function, and electronegativity for Pt, Pb, Sn, Cd, Ga, Ni and In.

Element	Work Function <sup>a</sup>	Electronegativity <sup>a,b</sup>
Pt	2.2	2.1
Pb	1.6	1.6
Sn	1.7	1.7
Cd	1.6	1.5
Ga	1.6	1.5
Ni	2.0	1.8
In		1.5

a. Reference 18.

b. The electronegativity values are mean values or probable values for the most common form of bonding of the given element.

TABLE II. Valence band properties in the Pt-Ga intermetallic compounds  
(all values in eV with respect to the Fermi level)

	Pt 5d Band Width	Ga 3d BE
Pt	9.2	
Pt <sub>2</sub> Ga	8.4	18.9
PtGa	8.0	18.9
PtGa <sub>2</sub>	7.4	19.1
Ga		19.0



TABLE III. Binding energies (in eV) of the Pt 4f , Ga 3s, and Ga 3p levels in the Pt-Ga intermetallic compounds.

	Pt 4f <sub>7/2</sub>	Pt 4f <sub>5/2</sub>	Ga 3p	Ga 3s	$\Delta E^a$
Pt <sub>2</sub> Ga	71.0	74.3	104.3	159.6	33.5
PtGa	71.0	74.3	104.1	159.4	33.1
PtGa <sub>2</sub>	71.1	74.5	103.7	159.0	32.6

a. Binding energy difference between Pt 4f<sub>7/2</sub> and Ga 3p peaks.

TABLE IV. Structures and Pt-Pt distances in the Pt-Ga intermetallic compounds.

compound	structure type	R (Pt-Pt) <sup>a</sup>	coordination number
Pt	cubic (f. c. c.)	2.77 (Å)	12
Pt <sub>2</sub> Ga	orthorhombic	2.77 (Å)	8 or 6 <sup>b</sup>
PtGa	FeSi (B20 type)	3.02 (Å)	6
PtGa <sub>2</sub>	cubic (CaF <sub>2</sub> )	4.19 (Å)	12

a. Shortest distance between Pt atoms.

b. Alternate Pt atoms are 8- or 6-fold coordinated.

## FIGURE CAPTIONS

Fig. 1. XPS valence band spectra from the Pt-Ga intermetallic compounds.

Fig. 2. Ga 3s, Ga 3p, and Pt 4f XPS spectra from the Pt-Ga intermetallic compounds, normalized to constant peak height and shifted to align the main peaks.

Fig. 1.

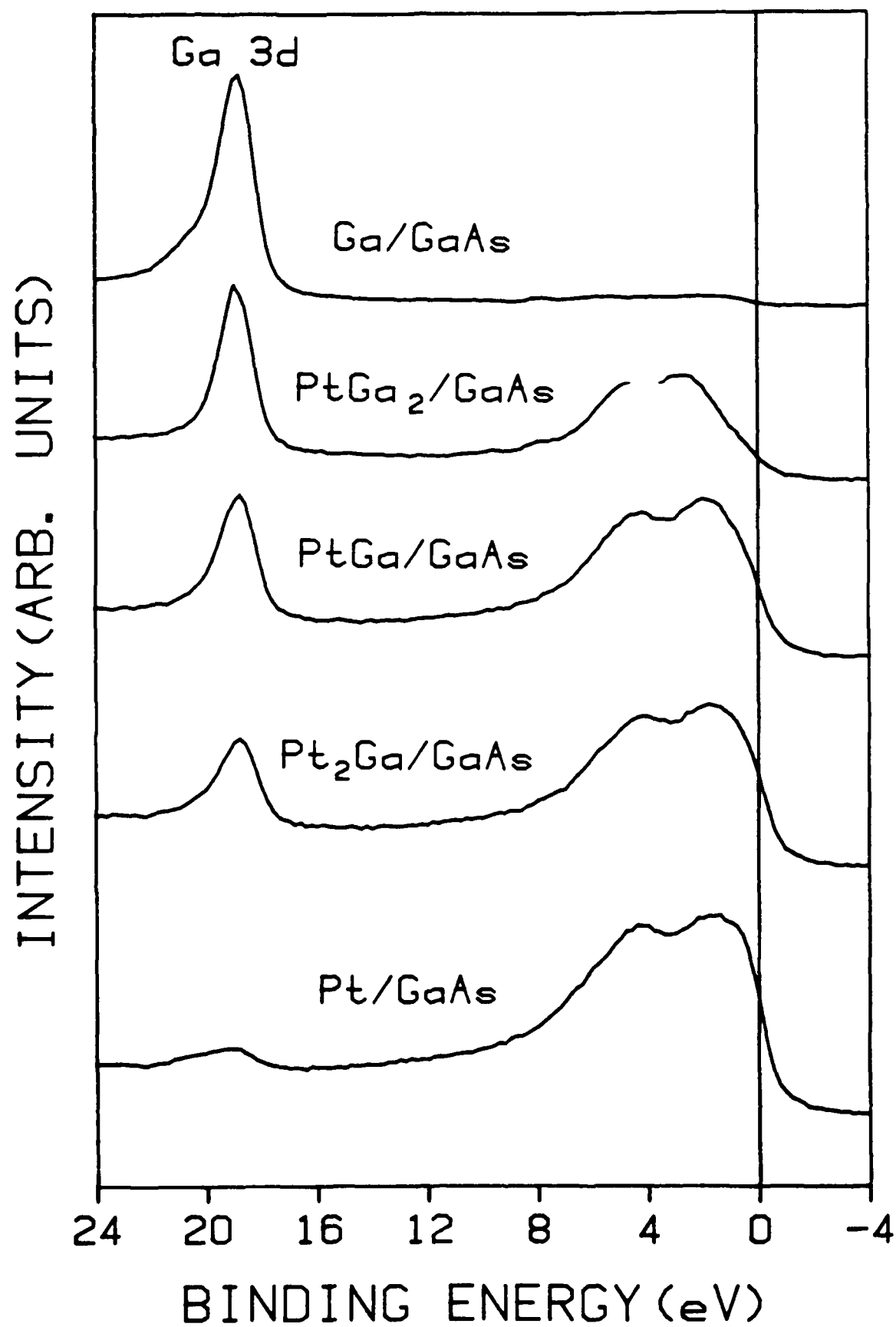


Fig. 2.

